NUCLEAR MAGNETIC RESONANCE STUDIES IN COORDINATION CHEMISTRY

VIII. THE INFLUENCE OF SOLVENT ON EXCHANGE REACTIONS INVOLVING THE SYSTEM [1,5-CYCLOOCTADIENE–RhCl]$_2$+AsPh$_3$

K. VRIEZE, H. C. VOLGER and A. P. PRAAT

Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research N.V.), (The Netherlands)

SUMMARY

NMR studies are reported on reactions involving the monomeric complex (COD)RhCl(AsPh$_3$)(COD = 1,5-cyclooctadiene) in CD$_2$Cl$_2$. The results are compared with those for CDCl$_3$ as solvent.

It is shown that both in CDCl$_3$ and CD$_2$Cl$_2$ ligand exchange reactions occur for mixtures of the monomer with free AsPh$_3$. The absolute rates are higher in the latter solvent.

The kinetic behaviour for mixtures of the monomer and the dimer [(COD)-RhCl]$_2$ differ widely for the two solvents. In CDCl$_3$ reactions occur between the dimer and an active intermediate "(COD)RhCl(AsPh$_3$)". In CD$_2$Cl$_2$ ligand dissociation and reactions of dissociated ligand with the monomer and the dimer, respectively, are dominant, while monomer–dimer reactions have also been observed.

INTRODUCTION
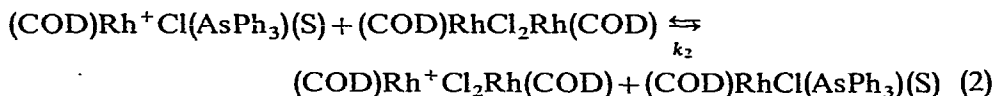
Previous reports of this series dealt with kinetic investigations—using NMR—on exchange reactions involving the monomeric π-methylallylpalladium compounds (π-C$_4$H$_7$)PdCl(L) (L = AsPh$_3$[1,2], PPh$_3$[1,3]) and the diene compounds (COD)RhCl(L)[4], (COD)IrCl(L)[5] (COD = 1,5-cyclooctadiene) and (Nor)RhCl(L)[6] (Nor = bicyclo[2,2,1]-hepta-2,5-diene). The kinetic behaviour was found to be particularly interesting for mixtures of the monomeric compounds with the parent dimer compounds, *i.e.* [(π-C$_4$H$_7$)PdCl]$_2$ and [(diene)MCl]$_2$.

In the case of the phosphine systems the monomers were found to react with the dimers and with species such as [(π-C$_4$H$_7$)PdCl] which result from dissociation of the dimer. The reactions observed in the arsine systems of π-methallylpalladium, cyclooctadieneiridium and norbornadienerhodium chloride, however, were found to involve reaction of dimer and monomer compounds, respectively, with free triphenylarsine, which is formed by dissociation of the monomer. The exception in the case of the arsine systems proved to be the 1,5-cyclooctadienerhodium system, where no formation of free AsPh$_3$ by dissociation occurred[4]. The observed dependence of the rates on concentrations was accounted for by adopting the following tentative reaction scheme.

A rate-determining formation of an active five coordinate species* ($CDCl_3 = S$):

$$(COD)RhCl(AsPh_3)(S)_2 \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} (COD)RhCl(AsPh_3)(S) + S \qquad (1)$$
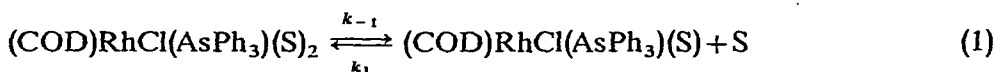
followed by a fast bimolecular reaction of the dimer with the active species, with exchange of $AsPh_3$ ($k_{-1} \ll k_2 \cdot [M_2]$):

$$(COD)Rh^+Cl(AsPh_3)(S) + (COD)RhCl_2Rh(COD) \underset{k_2}{\rightleftharpoons}$$

$$(COD)Rh^+Cl_2Rh(COD) + (COD)RhCl(AsPh_3)(S) \qquad (2)$$

Since the formation of the intermediate species**, which has to be assumed in view of the observed concentration dependencies of the rates, will obviously be strongly influenced by the solvent, we investigated the same system in CD_2Cl_2 which has a higher dielectric constant and dipole moment[7] than $CDCl_3$ and may thus be a better coordinating agent.

The results of kinetic measurements on the system in CD_2Cl_2 are presented in this report together with those for the system in $CDCl_3$, which has been completely reinvestigated under exactly the same reaction conditions. It is shown that the two systems differ widely in their kinetic behaviour.

EXPERIMENTAL

The preparation, properties and handling of the compounds $(COD)RhCl(L)$ ($L = AsPh_3$, PPh_3) and $[(COD)RhCl]_2$ have been reported before[4,8].

The NMR spectra were measured with an HA 100 Varian spectrometer with TMS (tetramethylsilane) as internal standard. The temperatures were carefully checked before and after each measurement. They are accurate within $\pm 1°$.

The methods of calculating the rates, which were all obtained for the slow exchange limit, and the accuracy of the results have been discussed in previous reports[4-6].

Results of the kinetic measurements

The results will be discussed for:
(A) mixtures of the monomer $(COD)RhCl(AsPh_3)$ and $AsPh_3$ (*i.e.* L/Rh > 1),
(B) mixtures of the monomer and the dimer $[(COD)RhCl]_2$ (*i.e.* L/Rh < 1),
(C) solutions of the pure monomer (*i.e.* L/Rh = 1).

In all cases the rates were measured for $CDCl_3$ and for CD_2Cl_2 as the solvent.

## (A) L/Rh > 1

The coalescence of the signals of protons H_A and H_B which, as shown before[4], is caused by a ligand exchange reaction between $(COD)RhCl(AsPh_3)$ and $AsPh_3$, could be studied at temperatures from $-80°$ to $-20°$. The reciprocal of the lifetime of protons H_A or H_B [$1/\tau(ML)$] is proportional to $[L]_0$ for constant $[ML]_0$, and

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* Two weakly coordinated solvent molecules (S), may be thought to occupy coordination positions above and below the plane of the monomer.
** Other possibilities for the structure of the intermediate have been discussed before.

independent of $[ML]_0$ for constant $[L]_0$ both in $CDCl_3$, as reported before[4], and in CD_2Cl_2 (Figs. 1 and 2). The proposed reaction is shown below:
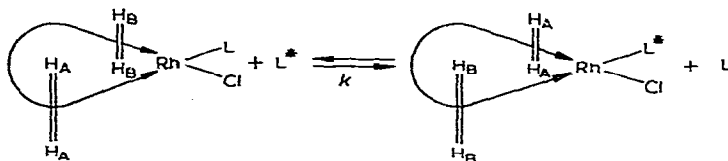
The reaction constants are $k(CDCl_3) = 10^{6.8} \cdot e^{-3900/R \cdot T}$ and $k(CD_2Cl_2) = 10^{6.6} \cdot e^{-3700/R \cdot T}$. The exchange proceeds in all probability via a five coordinate intermediate which is present in these solvents in negligible concentrations, as indicated by the observation that $1/\tau(ML)$ is independent of $[ML]_0$*. It is clear from Figs. 1 and 2 that the exchange reaction is about one and a half times as fast in CD_2Cl_2 as in $CDCl_3$.
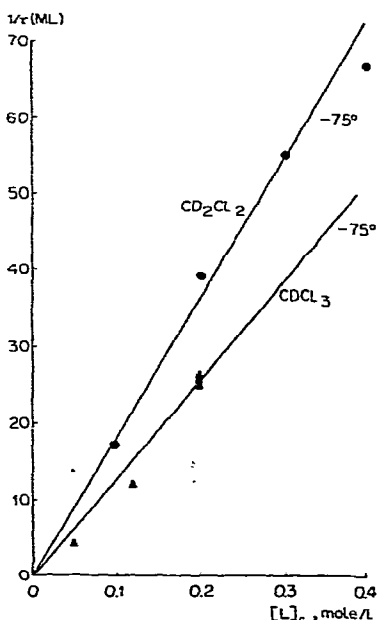

Fig. 1. The dependence of $1/\tau(ML)$ on $[L]_0$ for $[ML]_0 = 0.20$ mole/l $[ML = (COD)RhCl(L)$; $L = AsPh_3]$ in CD_2Cl_2 and $CDCl_3$.

At higher temperatures the log $1/\tau(ML)$ vs. T^{-1} lines have a tendency to level off, which is presumably due to an irreversible oxidation of the free ligand. No such behaviour was noted for $L/Rh < 1$ and $L/Rh = 1$.

(B) L/Rh < 1

The coalescence of the olefinic proton signals H_A and H_B of the monomer with H_C of the dimer for $CDCl_3$ solutions have been shown before (Fig. 5, ref. 4).

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* This further means that the equilibrium concentrations $[ML]$ and $[L]$ are approximately equal to $[ML]_0$ and $[L]_0$ (weighed-in quantities).
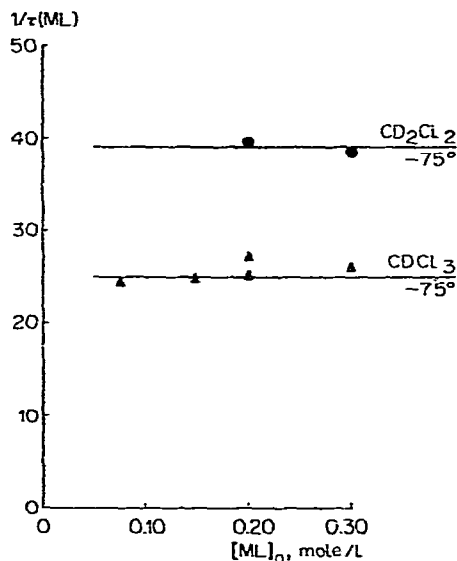
Fig. 2. The dependence of $1/\tau(ML)$ on $[ML]_0$ for $[L]_0 = 0.20$ mole/l $[ML(COD)RhCl(L)$; $L = AsPh_3]$ in CD_2Cl_2 and $CDCl_3$.

A similar coalescence was noted with CD_2Cl_2 as the solvent. These observations indicate a chemical exchange, *i.e.* monomer is converted into dimer and *vice versa*.

As the kinetic results for $L/Rh < 1$ are different for the two solvents, we will discuss the results separately.

1. *CDCl_3 as solvent.* It has been found previously[4] that with CDCl_3 as the sol-
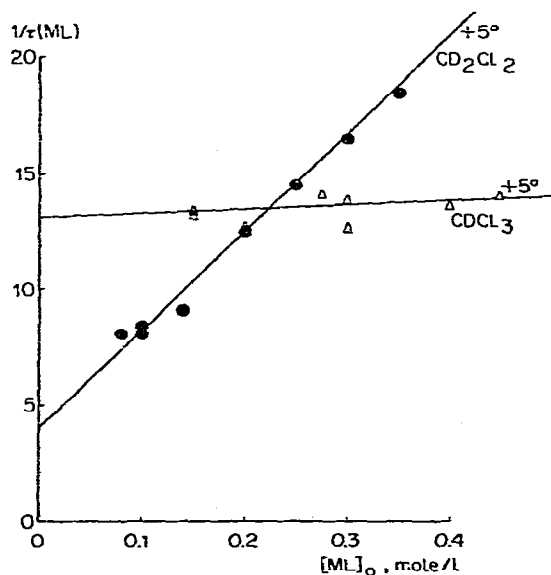

Fig. 3. The dependence of $1/\tau(ML)$ on $[ML]_0$ for $[M_2]_0 = 0.05$ mole/l $[ML = (COD)RhCl(AsPh_3)$; $M_2 = [(COD)RhCl]_2]$ in CD_2Cl_2 and $CDCl_3$.

vent the rates of the monomer $(COD)RhCl(AsPh_3)$ $(=ML)$ and of the dimer $[(COD)-RhCl]_2$ $(=M_2)$ depend on concentration as follows:

$$1/\tau(ML) = k_{obs}$$

$$1/\tau(M_2) = k_{obs} \cdot [ML]_0/[M_2]_0 .$$

The proposed mechanism involved reactions (1) and (2) with

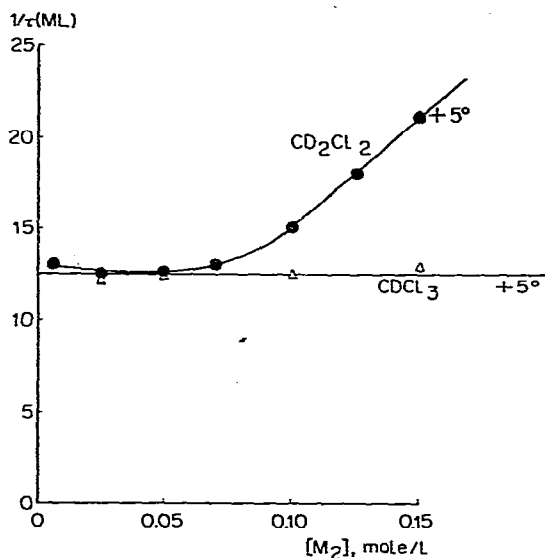$$k_{obs} = k_1 = 10^{13} \cdot e^{-15000/R \cdot T} \text{ sec}^{-1} \text{ *}.$$

Fig. 4. The dependence of $1/\tau(ML)$ on $[M_2]_0$ for $[ML]_0 = 0.20$ mole/l $[ML = (COD)RhCl(AsPh_3)$; $M_2 = [(COD)RhCl]_2]$ in CD_2Cl_2 and $CDCl_3$.

A careful reinvestigation of this system confirmed these findings (Figs. 3–6), although now a very small, but definite increase of $1/\tau(ML)$ with increasing $[ML]_0$ was observed (Fig. 3) when an HA 100 spectrometer was used instead of the somewhat less accurate DP 60. This very small increase of $1/\tau(ML)$ with $[ML]_0$ is very probably due to the onset of reactions of one monomer with the other:

$$(COD)Rh^+Cl(AsPh_3)^{\neq} + (COD)RhCl(AsPh_3) \overset{\rightleftharpoons}{\underset{k_3}{}}$$

$$(COD)Rh^+Cl(AsPh_3) + (COD)RhCl(AsPh_3)^{\neq} \quad (3)$$
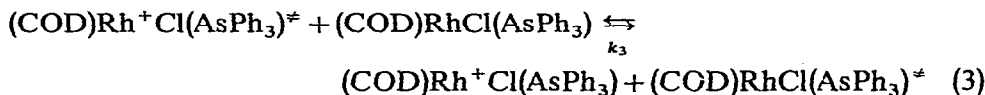
The rate expressions for reactions (1), (2) and (3) are:

$$1/\tau(ML) = k_1 + k_3 \cdot [ML]$$

$$1/\tau(M_2) = k_1 \cdot [ML]/[M_2]$$

2. *CD_2Cl_2 as solvent.* In the case of CD_2Cl_2 we observed, quite unexpectedly, completely different concentration dependencies. For the rate $1/\tau(M_2)$ the following

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* The observed k is now $10^{13} \cdot e^{-14000/R \cdot T}$ sec^{-1}, which is equal to the previous value within the experimental error.

dependency was found:

$$1/\tau(M_2) = k'_{obs} \cdot [ML]_0^2/[M_2]_0$$ 　　　　　　(Figs. 5 and 6)*

$$k'_{obs} = 10^{11} \cdot e^{-12000/R \cdot T} \ 1 \cdot mole^{-1} \cdot sec^{-1}$$

Much the same expression has been obtained earlier for the cyclooctadiene-iridium arsine system[5], in which ligand dissociation and ligand exchange reactions were the dominant features. The rate $1/\tau(ML)$ (about $10^{11} \cdot e^{-13000/R \cdot T}$ sec^{-1}), however, decreases slightly with $[M_2]_0$ for low dimer concentrations ($[ML]_0$ is kept constant), increasing again proportionally to $[M_2]_0$ for high dimer concentrations (Fig. 4). (*N.B.* dimer concentrations larger than 0.15 mole/l could not be used owing to its poor solubility). Furthermore, $1/\tau(ML)$ is proportional to $[ML]_0$ when $[M_2]_0$ is constant (Fig. 3); the straight line, however, does not pass through zero.
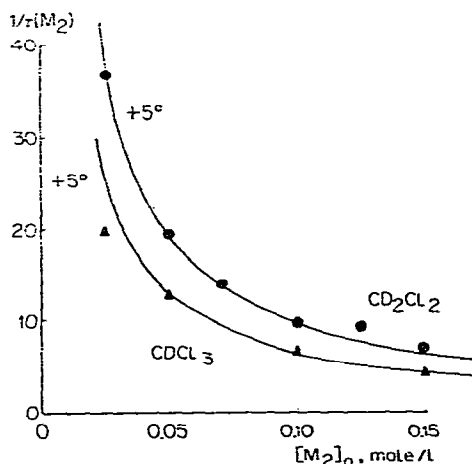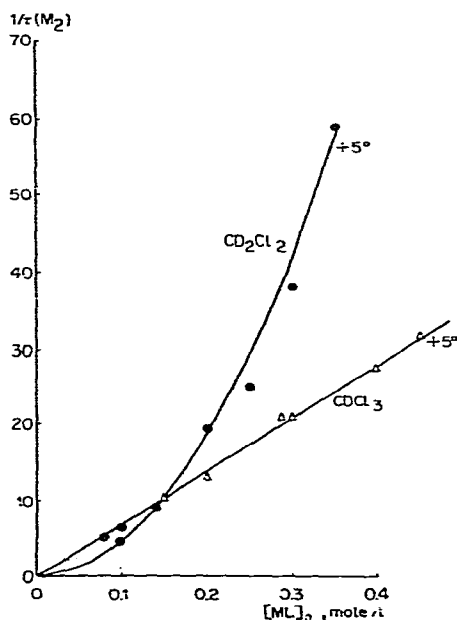

Fig. 5. The dependence of $1/\tau(ML)$ on $[ML]_0$ for $[M_2]_0 = 0.05$ mole/l [ML = (COD)RhCl(AsPh$_3$); M$_2$ = [(COD)RhCl]$_2$] in Cd$_2$Cl$_2$ and CDCl$_3$. The broken line for Cd$_2$Cl$_2$ represents a calculated $1/\tau(M_2)$ *vs.* $[ML]_0^2$ dependence.

Fig. 6. The dependence of $1/\tau(M_2)$ on $[M_2]_0$ for $[ML]_0 = 0.20$ mole/l [ML = (COD)RhCl(AsPh$_3$); M$_2$ = [(COD)RhCl]$_2$] in CD$_2$Cl$_2$ and CDCl$_3$. Both curves represent a calculated $1/\tau(M_2)$ *vs.* $1/[M_2]_0$ dependence.

The observed concentration dependencies may be explained by taking into account, besides reactions (1) to (3), also reactions (4) to (8). Dissociation of ML with formation of AsPh$_3$:

$$(COD)RhCl(AsPh_3) \underset{k_4}{\rightleftharpoons} (COD)RhCl + AsPh_3$$ 　　　　　　(4)
　　　　ML　　　　　　　　M　　　　L

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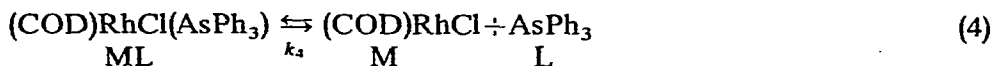
* $[ML]_0$ and $[M_2]_0$ are equal to the equilibrium concentrations $[ML]$ and $[M_2]$, respectively, within the limits of observation.

which is followed by reactions of $AsPh_3$ with dimer and monomer, respectively. The reaction with the dimer proceeds via two steps (5a) and (5b), of which (5b) must be rate-determining, in view of the concentration dependency of $1/\tau(M_2)$:

$$[(COD)RhCl]_2 + AsPh_3 \xrightleftharpoons[k_{5a}]{} (COD)RhCl(AsPh_3)ClRh(COD) \qquad (5a)$$
$$M_2 \qquad L \qquad\qquad\qquad M_2L$$

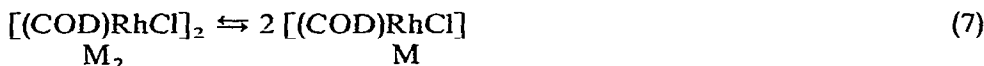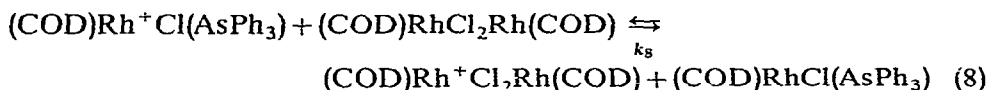$$[(COD)RhCl(AsPh_3)ClRh(COD) + AsPh_3 \xrightleftharpoons[k_{5b}]{} 2 (COD)RhCl(AsPh_3) \quad (5b)$$
$$M_2L \qquad\qquad\qquad L \qquad\qquad ML$$

$$(COD)RhCl(AsPh_3) + AsPh_3^+ \xrightleftharpoons[k_6]{} (COD)RhCl(AsPh_3^+) + AsPh_3 \qquad (6)$$
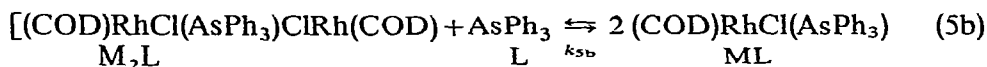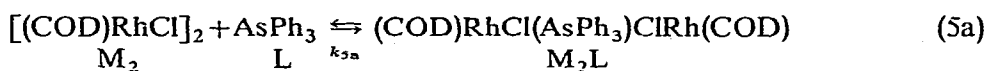
Dissociation of the dimer occurs according to:

$$[(COD)RhCl]_2 \rightleftharpoons 2 [(COD)RhCl] \qquad\qquad (7)$$
$$M_2 \qquad\qquad M$$

Besides these reactions there may also occur a direct reaction of monomer with dimer:

$$(COD)Rh^+Cl(AsPh_3) + (COD)RhCl_2Rh(COD) \xrightleftharpoons[k_8]{}$$
$$(COD)Rh^+Cl_2Rh(COD) + (COD)RhCl(AsPh_3) \quad (8)$$

The calculated rate $1/\tau(ML)$ is:

$$1/\tau(ML) = k_1 + k_3 \cdot [ML] + k_4 + k_6 \cdot (K_4/K_7^{\frac{1}{2}}) \cdot [ML]/[M_2]^{\frac{1}{2}} + k_8 \cdot [M_2]$$

and further

$$1/\tau(M_2) = k_1 \cdot [ML]/[M_2] + k_5 \cdot (K_4^2/K_7) \cdot [ML]^2/[M_2] + k_7 + k_8 \cdot [ML]$$

From the observed concentration dependency for $1/\tau(M_2)$ [Figs. (5) and (6)] it is obvious that reactions (5a) and (5b) are dominant. This means that in CD_2Cl_2 a small amount of free $AsPh_3$ is formed through dissociation, whereas in $CDCl_3$ this does not occur.

The presence of free $AsPh_3$ implies that reaction (6) has to be taken into account also. The simultaneous occurrence of reactions (6) and (8) explains the non-linear curve, which represents the dependence of $1/\tau(ML)$ on $[M_2]_0$ when $[ML]_0$ is constant (Fig. 4). The contributions of these reactions are represented by the fourth and fifth terms in the rate expression for $1/\tau(ML)$, which give an inverse proportionality to $[M_2]^{\frac{1}{2}}$ and a direct proportionality to $[M_2]$, respectively. At low concentration of $[M_2]$ the fourth term will be important, whereas at higher dimer concentration the fifth term will become more significant. At high concentration of M_2 a proportionality in $[M_2]_0$ is expected, and actually observed. If we consider the dependence of $1/\tau(ML)$ on $[ML]_0$ we see that this is explained satisfactorily by reaction (6), although reaction (3) may also contribute to the line broadening.

Whether reactions (1) and (2), which were the most important for $CDCl_3$ as the solvent, play a role in CD_2Cl_2 is not very clear. If they were important, we could expect the $1/\tau(ML)$ versus $[ML]_0$ line to intersect the $1/\tau(ML)$ axis at a higher point than it does (i.e. $\sim 4\ sec^{-1}$) (Fig. 3).

(C) L/Rh=1

As in section B, we will first discuss the results for $CDCl_3$ as solvent and subsequently those for CD_2Cl_2.

1. *CDCl$_3$ as solvent.* The rate $1/\tau(ML)$ is proportional to $[ML]_0$ (Fig. 7). However, comparison with $1/\tau(ML)$ values for mixtures of monomer and dimer (Fig. 3) at similar temperatures and monomer concentrations indicates that the rate $1/\tau(ML)$ for ML alone is only to a small extent due to monomer-monomer reactions [reaction (3)]. The other reaction(s) occurring are not yet known. It will be attempted to throw more light on these by further studies of the influence of solvents.
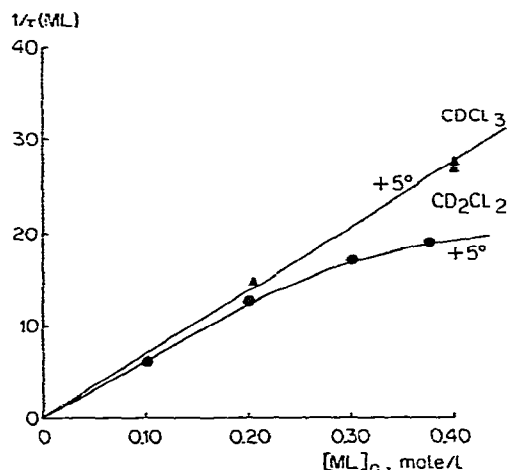

Fig. 7. The dependence of $1/\tau(ML)$ on $[ML]_0$ for ML alone in CD_2Cl_2 and $CDCl_3$. [ML = (COD)RhCl-(AsPh$_3$)].

2. *CD$_2$Cl$_2$ as solvent.* The rate $1/\tau(ML)$ as a function of $[ML]_0$ follows approximately a $[ML]_0^{\frac{1}{2}}$ curve. It seems likely therefore, in view of the observed ligand exchange for mixtures of monomer and dimer, that the dominant reaction here is the ligand exchange reaction (6). The AsPh$_3$ is formed by dissociation reaction (4). It has been shown before for solutions of (COD)IrCl(AsPh$_3$)[5] that the combination of these two reactions gives for $1/\tau(ML)$:

$$1/\tau(ML) = k_6 \cdot \sqrt{K_4 \cdot [ML]} \quad ([ML] = [ML]_0)$$

where $k_6 \cdot \sqrt{K_4} = 10^{10} \cdot e^{-10000/R \cdot T} \, l^{\frac{1}{2}} \cdot \text{mole}^{-\frac{1}{2}} \cdot \text{sec}^{-1}$
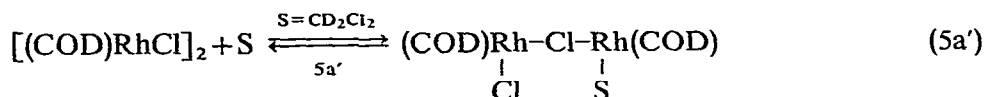
DISCUSSION

We will first discuss the results for mixtures of the monomer (COD)RhCl-(AsPh$_3$) and AsPh$_3$, and subsequently the data for mixtures of monomer and dimer and of solutions of the monomer alone.

It is clear that for reaction mixtures of (COD)RhCl(AsPh$_3$) and AsPh$_3$ bimolecular ligand exchange reactions occur both in CDCl$_3$ and in CD$_2$Cl$_2$. The five coordinate intermediate is present here in only a small amount, in contrast to the iridium systems[5]. The $1/\tau(ML)$ lines pass through zero (Fig. 1), which indicates that a ligand-independent solvent reaction path does not play an important role. This is not surprising because highly nucleophilic ligands prefer the ligand-dependent reac-
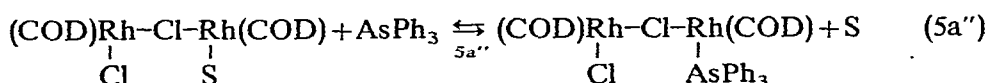
tion path. The ligand exchange reaction is about one and a half times as fast in CD_2Cl_2 as in $CDCl_3$. The differences between the activation parameters of the reactions in the two solvents are so small that no importance is attached to them.

For mixtures of monomer and dimer the reactions suggested for $CDCl_3$ as the solvent are (1), (2), with a small contribution by (3)*. The possible molecular configurations for the active intermediate have been discussed before[4]. In the case of CD_2Cl_2 clearly some free $AsPh_3$ is formed by dissociation, possibly because CD_2Cl_2 having a higher dipole moment**, is a better coordinating agent than $CDCl_3$. The $AsPh_3$ so formed reacts with the dimer in a two-step reaction (5a) and (5b), of which the second step must be slower than the first.
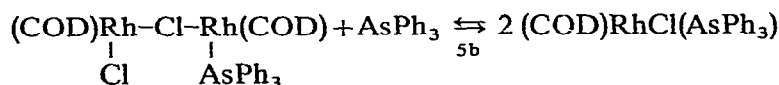
We suggest that in these reactions a pre-equilibrium is involved similar to the one suggested before for $[NorRhCl]_2$[9]:

$$[(COD)RhCl]_2 + S \underset{5a'}{\overset{S=CD_2Cl_2}{\rightleftharpoons}} \underset{\substack{| \\ Cl}}{(COD)Rh}-Cl-\underset{\substack{| \\ S}}{Rh(COD)} \qquad (5a')$$

The coordinatively unsaturated species (solvent S is weakly coordinated) is expected to be very reactive towards $AsPh_3$:

$$\underset{\substack{| \quad\quad | \\ Cl \quad\quad S}}{(COD)Rh}-Cl-Rh(COD) + AsPh_3 \underset{5a''}{\rightleftharpoons} \underset{\substack{| \quad\quad\quad | \\ Cl \quad\quad AsPh_3}}{(COD)Rh}-Cl-Rh(COD) + S \qquad (5a'')$$

The species so formed is coordinatively saturated and is expected to react more slowly with a second molecule of $AsPh_3$***:

$$\underset{\substack{| \quad\quad | \\ Cl \quad\quad AsPh_3}}{(COD)Rh}-Cl-Rh(COD) + AsPh_3 \underset{5b}{\rightleftharpoons} 2 (COD)RhCl(AsPh_3)$$

A similar reaction mechanism was proposed for the iridium system[5].

The kinetic results further show that the monomer $(COD)RhCl(AsPh_3)$ is involved in various reactions, of which the ligand exchange reaction (6) and the monomer–dimer reaction (8) are the most important. In addition, reactions (1), (2) and (3) may occur, but the kinetics indicate that they are not important.

In solutions of the monomer $(COD)RhCl(AsPh_3)$ alone in CD_2Cl_2 evidently

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* A more refined structure of the activated intermediate $(COD)RhCl(AsPh_3)(CDCl_3)$ may involve a partial loosening of the Rh–As bond. It should be noted that a dissociation of ML to a very small extent into M and L, with M and ML in the slow exchange and M and M_2 in the fast exchange, may give the same concentration dependencies for $1/\tau(ML)$ and $1/\tau(M_2)$. The concentration of L, however, must then be very small indeed, because the reaction of M_2 with L was not observed in $CDCl_3$. In the absence of further data we prefer, however, the above mechanism.

** The dipole moments of CH_2Cl_2 and $CHCl_3$ are 1.55 and 1.15 D[7], respectively; the dielectric constants are 9.08 and 4.81, respectively. The values for the deuterated compounds are expected to differ very little from those of the non-deuterated solvents.

*** Bridge splitting reactions of dimer with ligand may also be first order in L, as observed by Pearson and Muir[10]. The reaction mechanism involved a fast second step of ligand L with a coordinatively unsaturated monomeric species, whereas in our case the second step (5b) involves a reaction with a dimeric saturated species. It should be noted, as explained in Part II of this series[2], that for second-order behaviour it is sufficient that reaction 5a is in the fast exchange and 5b in the slow exchange.

reactions (4) and (6) occur. In $CDCl_3$ the nature of the reactions occurring besides (3) is not yet clear. It is hoped to elucidate these in the future.

The results for mixtures of monomer and dimer demonstrate that small differences in the nature of the solvents used may have a considerable effect on the type of reactions occurring.

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